COMPLETE SPECIFICATION

Alkylation of benzene

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des
5 Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and
10 by the following statement:—

This invention relates to an alkylation process for producing the reaction product between benzene and an olefin hydrocarbon. It specifically relates to the production of
15 benzene mono-alkylates suitable for conversion to a detergent product.

It has long been known that the satisfactory disposal of sewage and the inactivation of detergents dissolved in sewage is a
20 difficult but extremely necessary processing problem. Many of the detergents, for example, those having an alkylaryl structure as the organic portion tend to produce stable foams in hard or soft waters in such large
25 quantities that such foam clogs sewage treatment facilities and destroys the bacteria necessary for sufficient biological action for proper sewage treatment. It is also known that the alkylbeneze sulfonates (ABS) deter-
30 gents, which are prepared by alkylating benzene with propylene-tetramer alkylating agent, are not readily biodegraded in modern sewage treatment plants. The prior art has also known tht biodegradable linear alkyl-
35 benzene sulfonates (LAB) are most desirable in the commercial market today. Present methods for producing the biodegradable detergents utilize normal paraffins as a source of the straight chain alkyl substitu-
40 ents. Heretofore, the prior art processing scheme for producing LAB have included: chlorination followed by direct alkylation of benzene with the alkylchlorides using

aluminum chloride as the catalyst; chlorina-
tion followed by dehydrochlorination and 45
alkylation of benzene with the resultant
olefins using an acid catalyst; and the crack-
ing of higher molecular weight paraffinic
hydrocarbons such as waxes to form suitable
olefins which are then used to alkylate ben- 50
zene with an acid catalyst.

It can thus be seen that the most popular
prior art schemes involve several rather
complicated processing steps. However,
more recently there has been discovered a 55
process in which normal paraffins are made
in sufficient purity for direct catalytic de-
hydrogenation of the n-paraffins to the cor-
responding n-mono-olefins of the same car-
bon number. Basically, this most recent 60
prior art process involves the extraction of,
for example, kerosene to produce n-paraffins
of extremely high purity. These high purity
n-paraffins are catalytically dehydrogenated
to n-olefins. The dehydrogenation effluent 65
is admixed with benzene and converted to
alkylbenzene in the presence of an acid cata-
lyst such as hydrogen fluoride. The alkyla-
tion effluent is separated into linear alkyl-
benzenes and a by-product heavy alkylate. 70
The excess n-paraffins are usually recycled
to the dehydrogenation section. Similarly,
any excess benzene is recycled to the alkyla-
tion reacton zone.

The present invention is an improved 75
method of performing the alkylation reaction
of, for example, the hereinabove described
most recent prior art method for producing
bidegradable linear alkylbenzene sulfonates.

Therefore, it is an object of the present 80
invention to provide a process that can be
used for the preparation of a linear alkylated
benzene mono-alkylate suitable for conver-
sion to a detergent product.

It is a specific object of this invention to 85
provide a method which can be used for

[Price 5s. 6d.]

producing an alkylated benzene mono-alkylate having a Bromine Index of less than 30 suitable for conversion to a detergent product.

Accordingly, the present invention provides a process for the preparation of alkylated benzene which comprises:

  a. reacting benzene with an olefinic hydrocarbon feed stream . in the presence of a catalyst comprising a mineral acid in a first reaction zone at a temperature within the range from 4 to 49°C.,

  b. separating from the effluent from said first reaction zone a first catalyst phase and a first hydrocarbon phase which includes unreacted olefinic hydrocarbon,

  c. returning at least a portion of said first catalyst phase to the first reaction zone as a portion of said acid catalyst,

  d. introducing said first hydrocarbon phase into a second reaction zone maintained at a temperature at least 3.6°C. higher than in the first reaction zone and therein further reacting said hydrocarbons in the presence of fresh acid catalyst,

  e. separating from the effluent from said second reaction zone a second catalyst phase and a second hydrocarbon phase comprising alkylated benzene,

  f. returning at least a portion of said second catalyst phase to the first reaction zone as a portion of said acid catalyst, and

  g. recovering resulting alkylated benzene.

In another embodiment of the present invention, a portion of the first acid phase is regenerated and returned to the second reaction zone as at least part of the fresh acid.

The feedstock for the alkylation reaction of the present invention is primarily a linear mono-olefin which, preferably, has been prepared by the direct dehydrogenation of its corresponding n-paraffinic precursor. Typically, the olefin feedstock to the alkylation reaction contains from 10 to 15 carbon atoms per molecule, preferably, from 11 to 14 carbon atoms per molecule. This linear mono-olefin is utilized as an alkylating agent for benzene. By operating in the manner taught by the present invention, exceptionally high yields of the desired mono-alkylate may be obtained.

The alkylation reaction is effected in the presence of a catalyst capable of promoting the condensation reaction. The catalyst is a mineral acid which catalyzes the alkyl-transfer reaction involved in the method of the present invention. Suitable catalysts include sulfuric acid containing not more than about 15% by weight of water and, preferably, less than about 8% by weight of water including used sulfuric acid cata-

lyst recovered from the alkylation of iso-paraffin hydrocarbons with mono-olefin hydrocarbons. Also suitable are hydrofluoric acid catalysts of at least 83% by weight concentration and containing, preferably, less than about 10% by weight of water, and liquified anhydrous hydrogen fluoride. The catalyst particularly preferred for the present alkylation reaction is hydrogen fluoride containing at least 83% by weight and, more preferably, at least 90% by weight hydrogen fluoride.

It is to be noted that one of the essential concepts of the present invention involves the utilization of catalyst in the first stage of the alkylation reaction zone which has been previously used in the second stage of such reaction zone. Thus, in effect, the catalyst is flowing in countercurrent manner to the flow direction of the hydrocarbon reactants. It is also to be noted that the first stage reaction zone is operated at a lower temperature than the second stage. By maintaining a relatively low temperature in the first stage, undesirable side reactions such as polymerization reactions are minimized. However, it was found that the low temperature desirable for the first stage reaction had the effect of producing undesirable quantities of alkylfluorides which act as a contaminant in the hydrocarbon product produced. Accordingly, the relatively high temperature maintained in the second stage of the reaction zone at least partially decomposes any alkylfluorides, thereby producing a reaction product at extremely high purity and in exceptionally high yield. In addition, it must be noted that the detergent industry requires that the linear alkylated benzene substantially be colorless, and in the substantial absence of olefinic contaminants. Accordingly, the Bromine Index of the alkylate produced must be less than 30 and, preferably, should be approximately 10, although, in some cases a Bromine Index of from 10 to 20 may be satisfactory. As a rough approximation, Bromine Index is approximately equal to the parts per million (ppm) of olefin hydrocarbons present in the product. It has been found that satisfactory color sulfonates may be produced if the mono-alkylate has a standard color comparator index (APHA) of less than 15 and, preferably, less than 10. Typically, in the practice of this invention, the desired mono-alkylate produced will have an APHA color of about 5.

As will become evident from the operating conditions presented hereinbelow it is preferable to operate the first stage alkylation zone of the present invention so that the consumption of the n-olefin alkylating agent is substantially complete. By this is meant that the olefin hydrocarbon should be consumed to an extent of at least 98% by weight, but

less than 100%. In similar manner, the operating conditions of the second stage of alkylation should preferably be chosen so that the remaining olefin agent is completely consumed and any alkylfluoride compounds present in the effluent from the first stage be at least partially decomposed. In a typical operation of the present invention, the olefin hydrocarbon is ultimately consumed in an amount of 99.9% by weight.

It was found that by operating in the manner of the present invention the second stage reaction was an exceptionally clean reaction in that only a small amount of tar contaminant was produced in the catalyst phase thereby reducing to a minimum the chances of contaminating the desired mono-alkylate product with off-color material such as entrained tar and/or polymerization products. In addition, it was found that the partially deactivated acid catalyst from the second stage reaction was eminently suitable to perform the catalytic reaction required in the first stage reaction zone, to wit: effecting a substantially complete reaction between the olefin hydrocarbon and benzene.

In the practice of the present invention the temperature in the first reaction zone is maintained at a relatively low level of 4°C. to 49°C., typically about 38°C. This may be achieved either by suitable heat exchange means, such as water cooling within the reactor or by prechilling the reactants and catalyst, so that the reaction medium will be at the appropriate low temperature. The operating conditions in the first reaction zone preferably include a residence time within a range of from 5 minutes to 25 minutes, typically, about 15 minutes; and a catalyst-to-hydrocarbon volume ratio within a range of from 0.2:1 to 10:1, typically, about 2:1. In order to maximize the production of the desired mono-alkylate from the alkylating agent charged to the process, it is generally preferred that the molar ratio of benzene-to-alkylating agent be greater than 1:1 and, more preferably, within the range from 2:1 to 15:1 mols per mol. Alternatively, it is distinctly preferable that a molar ratio of benzene-to-(olefin hydrocarbons plus alkylate product) be maintained at least as high as 3:1 and, typically, should be about 8:1. The upper limit for this ratio, of course, will be dictated by the economics of the process.

As previously mentioned, the operating conditions for the second reaction zone include a temperature which is at least 3.6°C. higher than the temperature maintained in the first reaction zone. Accordingly, these preferable operating conditions include a temperature within a range of from 27°C. to 66°C. typically about 49°C.; a residence time within a range of from 5 minutes to 25

minutes, typically, about 15 minutes; and an acid catalyst-to-hydrocarbon volume ratio within a range of from 0.2:1 to 10:1, typically, about 1:1. The benzene-to-(olefin hydrocarbon plus alkylate product) ratio should preferably be maintained greater than 2:1 in the second reaction zone, and, typically, will be about 7:1.

With reference to the acidity of the catalyst (the percent HF) in the practice of this invention, the control point for acidity is preferably the weight percent acid in the drag stream charged to the catalyst regeneration zone, as more fully discussed with reference to the appended drawing. The acidity of the acid catalyst in the first reaction zone may be from 86% to 92% by weight and, typically, will be about 90%. Acidities above and below this range may in some cases be used satisfactorily; although, in virtually no case should the acidity of the acid be allowed to drop below about 83% by weight. Similarly, for the second reaction zone the acidity of the acid catalyst should be greater than 90%, say, from 93% to 100% by weight, and typically, will be between 93% and 94% by weight. As used herein for convenience, it is to be noted that the term " fresh catalyst " is intended to embody both new catalyst brought in external to the process as well as regenerated catalyst coming from the catalyst regeneration zone. It also includes " used " sulfuric acid catalyst recovered from the alkylation of isoparaffins with mono-olefins. Preferably, the catalyst passed to the catalyst regeneration zone will be about 90% by weight so that the regenerated catalyst can conveniently be about 94% by weight.

The invention may be more fully understood from the following discussion with reference to the appended drawing, which is intended to be illustrative of one embodiment of the present invention and not intended as limiting the broad scope thereof. A n-paraffin hydrocarbon stream having a purity of about 98% and a carbon number range from 11 to 14 is passed into the process via line 10 where, if desirable, it is admixed with additional recycle n-paraffin feed from line 11. The entire feed stream is passed into dehydrogenation zone 12 which is a fixed bed catalytic unit operating at relatively mild conditions of temperature and pressure. For example, the operating conditions for dehydrogenation zone 12 include a temperature of about 466°C. and a pressure of about 2.0 atmospheres, gauge. Sufficient hydrogen is added to the system so that a mole ratio of hydrogen-to-combined feed of about 8 is maintained. Preferably, approximately 2,000 parts per million of water is present in the combined feed stream to dehydrogenation zone 12. A product

stream of corresponding linear olefin hydrocarbon comprising approximately 95% mono-olefins is removed from zone 12 via line 13. Of the remaining 5% of the material in line 13, the major portion is dienic with minor amounts of benzene. A by-product of the hydrogenation reaction is hydrogen of over 96% purity which is removed from zone 12 by means not shown.

The catalyst which is used in the dehydrogenation zone 12 is one which promotes the dehydrogenation of the paraffins to the mono-olefins without isomerization of the normal paraffins or the resulting mono-olefins without isomerization of the normal paraffins or the resulting mono-olefins to the corresponding branched chain analog. Suitable catalytic agents which minimize isomerization are the neutral oxides of the elements of Group VI and metal sulfides and/or oxides of the metals of Group VIII of the Periodic Table. The preferable catalyst for dehydrogenating the straight chain paraffin hydrocarbons comprise the noble metals or metal compounds such as platinum and/or palladium deposited on a neutral or basic support such as alumina.

The effluent from dehydrogenation zone 12 in line 13 is admixed with benzene from line 14, and the mixture of mono-olefins and benzene is passed via line 15 into first alkylation reaction zone 16. The effluent from the first alkylation reaction zone is withdrawn via line 17 and passed into separation zone 18 wherein suitable settling is performed in order to separate the acid catalyst phase from the hydrocarbon phase. The acid catalyst phase is removed from separation zone 18 via line 20 and returned to the first reaction zone in admixture with the feed in line 15. A drag stream of relatively spent acid catalyst is withdrawn as necessary from line 20 and passed via line 21 into catalyst regeneration zone 22.

The operating conditions necessary for catalyst regeneration are well known to those skilled in the art. The regeneration is normally accomplished by hydrocarbon vapor stripping of the acid catalyst under conditions sufficient to decompose alkylfluorides and to remove regenerated acid catalyst as a vapor product. The residual tarry material is withdrawn from catalyst regeneration zone 22 via line 23 and passed to a disposal unit not shown. The regenerated catalyst (herein also termed fresh catalyst) is withdrawn from zone 22 and passed via line 24 into admixture with the hydrocarbon phase being passed from separation zone 18 via line 19.

Referring again to separation zone 18, the separated hydrocarbon phase now substantially acid-free is withdrawn via line 19 and passed into heating means 26 where its temperature is raised at least 3.6°C. above the temperature maintained in the first reaction zone 16. The heated hydrocarbon phase and acid catalyst is passed via line 33 at a relatively high temperature into second alkylation reaction zone 27. Make-up catalyst as needed is added to the process via line 25.

The effluent from the second alkylation reaction zone is withdrawn via line 28 and passed into separation zone 29 wherein a separation between the acid and hydrocarbons is effected. The separated acid phase is withdrawn from separation zone 29 and passed via line 31 into second reaction zone 27 in admixture with the feed to the second reaction zone in line 33. A portion of the partially deactivated acid catalyst in line 31 is passed via line 32 and line 20 for return to the first reaction zone 16. Thus, it is to be noted that a portion of the acid catalyst for the first reaction zone is partially deactivated catalyst which had previously been used in the second reaction zone.

The hydrocarbon phase from separation zone 29 is passsed via line 30 to the recovery facilities not shown. A mono-alkylate product having a Bromine Index of less than 30 and, typically, between 10 and 20, is recovered from the material in line 30.

From the description presented herein, it can be seen that one embodiment of the present inventive process is characterized by two reaction zones with each zone having its separate circulating catalyst system and further characterized whereby the acid catalyst in the first reaction zone was obtained solely from the second reaction zone.
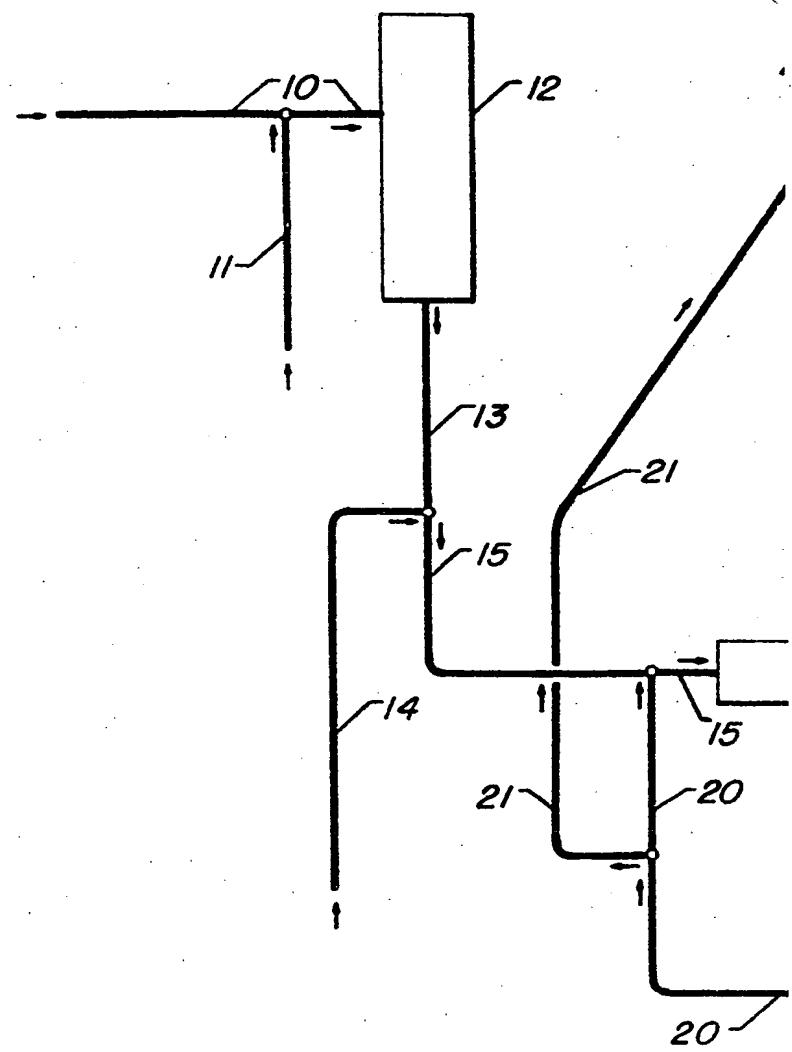
WHAT WE CLAIM IS:—

1. A process for the preparation of alkylated benzene which comprises:
   a. reacting benzene with an olefinic hydrocarbon feed stream in the presence of a catalyst comprising a mineral acid in a first reaction zone at a temperature within the range from 4 to 49°C.,
   b. separating from the effluent from said first reaction zone a first catalyst phase and a first hydrocarbon phase which includes unreacted olefinic hydrocarbon,
   c. returning at least a portion of said first catalyst phase to the first reaction zone as a portion of said acid catalyst,
   d. introducing said first hydrocarbon phase into a second reaction zone maintained at a temperature at least 3.6°C. higher than the first reaction zone and therein further reacting said hydrocarbons in the presence of fresh acid catalyst,
   e. separating from the effluent from said second reaction zone a second catalyst phase and a second hydrocarbon phase comprising alkylated benzene,
   f. returning at least a portion of said second catalyst phase to the first re-

action zone as a portion of said acid catalyst, and

g. recovering resulting alkylated benzene.

2. The process of claim 1, further characterized in that the second reaction zone is maintained at a temperature within a range of from 27°C. to 66°C.

3. The process of claim 1 or 2, further characterized in that a portion of the first catalyst phase is withdrawn, regenerated, and returned to the second reaction zone as a portion of the fresh catalyst.

4. The process of any of claims 1 to 3, further characterized in that the remainder of the second catalyst phase is returned to the second reaction zone.

5. The process of any of claims 1 to 4, further characterized in that the olefinic hydrocarbon feed stream comprises straight-chain mono-olefins having from 10 to 15 carbon atoms, and the mineral acid catalyst comprises hydrogen fluoride.

6. The process of any of claims 1 to 5, further characterized in that the first and second reaction zones are operated at a residence time of from 5 to 25 minutes and a catalyst-to-hydrocarbon volume ratio of from 0.2:1 to 10:1.

7. The process of any of claims 1 to 6, further characterized in that the alkylation is effected in the presence of an excess of benzene.

8. A process for preparing alkylated benzene according to claim 1 and substantially as hereinbefore described.

9. Alkylated benzene whenever produced in accordance with the process of any of the foregoing claims.

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